that electrochemical data have been reported for the $[M_2OCl_{10}]^{4-}$ species with M = Ru or Os.

To conclude this report, we shall discuss the spectroscopic and electrochemical data for this compound in the light of an appropriate form of the bonding scheme for the linear, dinuclear, oxo-bridged species. The well-known scheme originally put forward by Dunitz and Orgel[16] for the $[Ru_2OCl_{10}]^{4-}$ ion, which has D_{4h} symmetry, can easily be modified if we idealize the symmetry of the $Os_2OP_4Cl_6$ skeleton of our molecule to D_{2h}, using as before the M–O–M direction as the z axis and calling the plane containing the phosphorus atoms the xz plne and the one containing the four equatorial chlorine atoms the yz plane. The principal consequence of changing from a D_{4h} $[M_2OCl_{10}]^{4-}$ unit to a D_{2h} $M_2OP_4Cl_6$ unit is that the degeneracies of the e_u and e_g orbitals are lifted, e_u splitting into $b_{2u} + b_{3u}$ and e_g into $b_{2g} + b_{3g}$.

As far as the electrochemistry is concerned, the details of these splittings, so long as they are not large, are unimportant. We are still dealing with a system in which the LUMO is an orbital that is π antibonding with respect to the Os–O–Os unit and the HOMO is one of a set of approximately nonbonding orbitals. Reduction of the molecule places an electron in an antibonding (π^*) orbital, which accounts for the instability of the reduced species. Further reduction places still another electron in a set of π^* orbitals already singly occupied, and thus the very negative potential (−1.13 V) is not surprising, nor is the fact that this step is irreversible. Somewhat surprising is the high oxidation potential of +1.62 V. Thus, the HOMO may be more bonding in character than the qualitative picture of the electronic structure suggests. For $Os_2O(CH_3CO_2)_2(PR_3)_2$ species two voltammetric reductions were found at ca. +0.2 V (reversible) and −0.7 to −1.0 V (irreversible) with exact values depending on the identities of R and X.

While the electronic absorption spectrum (Figure 4) shows quite discrete, symmetrical bands, it is impossible to propose firm assignments, not only because of the low molecular symmetry but also because the spectrum of the obvious reference species $[Os_2OCl_{10}]^{4-}$ is poorly characterized.[7b,18] It appears that dissociation (or some other type of disintegration) of the dinuclear species occurs rapidly in solution, thus creating uncertainty as to what spectral features genuinely belong to the $[Os_2OCl_{10}]^{4-}$ ion. From the work of San Filippo, Fagan, and DiSalvo,[7b] however, it does appear that there is a band at 558 nm that must be associated with the Os–O–Os group and probably also another at 395 nm. For the more stable $[Ru_2OCl_{10}]^{4-}$ ion the spectrum is well-defined and there is good evidence that a band at 480 nm is due to a transition in the Ru–O–Ru group. San Filippo et al. suggest that it can be assigned to the e_g(π-nonbonding) to e_u(π-antibonding) transition.

The spectrum of $Os_2O(dppm)_2Cl_6$ is rather similar to that of $[Ru_2OCl_{10}]^{4-}$ except that instead of a broad band at 375 nm (ϵ = 10000) and another at 480 nm (5200) in the ruthenium compound there are three strong bands, as shown in Figure 4. Both compounds have a weak band in the near-IR, as does $[Os_2OCl_{10}]^{4-}$. Perhaps one or both of the strong bands characteristic of the $[M_2OCl_{10}]^{4-}$ ions have been split (by 3000–5000 cm^{-1}) by the change from a D_{4h} Os_2OCl_{10} central group to a D_{2h} $Os_2OP_4Cl_6$ central group.

Acknowledgment. We are grateful to The Robert A. Welch Foundation for financial support under Grant No. A-494.

Registry No. 1, 87883-13-4.

Supplementary Material Available: Details of the crystal structure determinations, tables of structure factors and anisotropic thermal parameters, complete lists of bond distances and bond angles, and tables of least-squares planes and torsional angles (30 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of Iron(II), Cobalt(II), and Nickel(II) Mono Complex Formation with Acetohydroxamic Acid

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The temperature-jump method has been used to determine the rate constants for the formation of complexes of Fe(II), Co(II), and Ni(II) in aqueous solution with bidentate acetohydroxamic acid at ionic strength 0.10 M ($NaNO_3$). The formation rate constants for reaction of the uninegatively charged, deprotonated form of ligand with Ni(II) and Co(II) are consistent with the dissociative (Eigen) mechanism of octahedral substitution. They are, at 20.0 ± 0.1 °C, for Ni(II) and Co(II) complex formation, $(3.25 \pm 1.18) \times 10^4$ and $(4.69 \pm 1.17) \times 10^6$ M^{-1} s^{-1} and, for complex dissociation, 1.63×10^{-1} and 3.21×10 s^{-1}, respectively. For reaction of Ni(II) and Co(II) at the same temperature with the neutral, protonated form of the ligand the formation rate constants are $(7.17 \pm 0.08) \times 10^2$ and $(3.59 \pm 0.08) \times 10^4$ M^{-1} s^{-1} and the dissociation rate constants are 8.03×10^6 and 6.38×10^8 M^{-1} s^{-1}, respectively. The complex formation and dissociation rate constants for reaction of the protonated form of ligand with Fe(II) at 10 ± 1 °C are 6.69×10^4 and 2.37×10^9 M^{-1} s^{-1}. Complex formation with the protonated form of ligand for all three ions is slower than that predicted by the Eigen mechanism: this effect is most likely due to rate-determining proton transfer from ligand to solvent.

The role of hydroxamic acid containing molecules in metal ion complexation is receiving much attention due to its clinical and biological significance.[1,2] The hydroxamic acid group is the moiety responsible for Fe(III) complexation in many siderophores, including the linear and cyclic ferrioxamines, ferrichromes, and aerobactin. The hydroxamate-containing chelator ferrioxamine B is used to treat acute iron toxicity.[3] The kinetics of interaction of Fe(III) with acetohydroxamic

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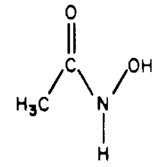
acid (HL) has been determined.[4,5] Interactions with divalent



acetohydroxamic acid

cations have received less attention; however, it has recently been shown that hydroxamic acid containing peptides are potent inhibitors of a broad class of divalent cation-containing peptidases, particularly those containing Zn(II), as a result of their ability to chelate these metal ions.[6]

Experimental Section

Fisher reagent grade nitrate salts of sodium(I), cobalt(II), and nickel(II) were used. Bromothymol blue, cresol red, and reagent grade ferrous sulfate were also from Fisher. Acetohydroxamic acid was from Aldrich. All chemicals were used without further purification. Doubly distilled water was used in all experiments. The ionic strength was brought to 0.1 M with $NaNO_3$. The pH was adjusted with dropwise addition of NaOH or HNO_3 solutions and monitored with an Orion digital ionalyzer, Model 801A. The hydrogen ion concentration was determined by dividing the measured hydrogen ion activity by $\gamma_\pm$ = Orion obtained from the Davies equation.[7] The pH meter was standardized with Fisher "Gram-pac" pH 6.86 phosphate buffer.

Kinetics experiments were performed at 20.0 ± 0.1 °C for Ni(II) and Co(II) and at 10 ± 1 °C for Fe(II) with a temperature-jump apparatus previously described,[8] but modified with a 150-W tungsten–halogen lamp for higher sensitivity. Relaxations were followed spectrophotometrically at 560 nm both near the λ_{max} of the more strongly absorbing form of indicator and also near the wavelength of highest photomultiplier sensitivity. Stock solution of indicator was added to solutions sufficient to obtain absorption at 560 nm of approximately 0.85 for optimum signal to noise ratio.[9] Traces indicating the change in percentage transmittance were recorded on a Tektronix 545A memory oscilloscope and subsequently photographed. Relaxation times are the average of at least four temperature jumps. The relative error for these sets of experiments is typically ±10%.

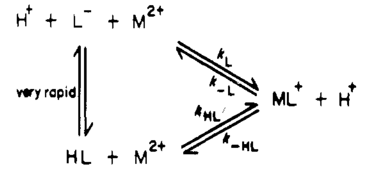
Calculation of chemical species distribution was determined with the program COMICS.[10] Rate constant and mechanistic analyses were performed through the use of a PDP-10, PDP-11/03, or PDP-11/23 computer system.

Control experiments were done at each pH region for metal–indicator and ligand–indicator combinations; no relaxations were seen in the time range of the metal–ligand processes. The oscilloscope traces were plotted semilogarithmically to test for the presence of one relaxation process. Plots were linear to beyond 3 relaxation times.

Solutions of these complexes with Ni(II) show the well-known pale green color of octahedral Ni(II) complexes and are therefore assumed to be in this configuration. Addition of ligand to aqueous Ni(II) solutons caused a pH drop of several units but no color change, indicating that complexation had occurred and that the electronic environment of Ni(II) was little perturbed by this ligand.

A few experiments were performed to obtain rate constants for complexation with Fe(II). Mixtures of ferrous sulfate, acetohydroxamic acid, and supporting electrolyte were prepared in a drybox under a nitrogen atmosphere and loaded into a 150-mL fritted column with $^1/_2$ g of finely powdered platinum black. Hydrogen gas was bubbled through the column for 10–15 min to generate H atoms and thereby the ferrous complex. The initial solution, in the absence of indicator, was pale red from the presence of small amounts of contaminating Fe(III). After a few minutes of hydrogen bubbling the solution turned clear, indicating Fe(II) had formed. Addition of indicator, pH adjustment, chilling of solution, and filling of the temperature-jump cell were all performed in the glovebox. The solution was immediately temperature jumped from 1 to 10 °C. Earlier experiments near room temperature showed a perturbation that was too fast to be resolved. Also, solution cavitation obscures the first 50–100 μs of the experiment near room temperature. Around 4 °C cavitation is eliminated and a relaxation was observed. These experiments were performed only at pH 7.1. Hydrolysis of slowly forming Fe(III), as a result of small amounts of oxygen contamination while the samples were in the temperature-jump apparatus, made these experiments difficult to perform; they were therefore only carried out under one set of conditions.

Scheme I



(I)

Table I. Stoichiometric Equilibrium Constants at Ionic Strength 0.1 M and 20 °C

Stability Constants[a] (M^{-1})

metal ion	K_{ML}[b]	metal ion	K_{ML}[b]
Fe(II)	6.31×10^4	Ni(II)	2.00×10^5
Co(II)	1.26×10^5		

Acid Dissociation Constants (M)

bromothymol blue[c]	7.94×10^{-8}
cresol red[c]	5.62×10^{-9}
acetohydroxamic acid[a]	4.47×10^{-10}

[a] Anderegg, G.; L'Eplattenier, F.; Schwarzenbach, G. *Helv. Chim. Acta* 1963, *46*, 1409. [b] $K_{ML} = [ML^+]/([M^{2+}][L^-])$. [c] Bishop, E. "Indicators"; Pergamon Press: New York, 1972.

Results

The reactions studied were of the type given in Scheme I, where L^- is the acetohydroxamic anion and M = Fe, Co, or Ni.

The stability constants for these complexes have been determined[11] and corroborated[12] and are collected along with other relevant equilibria in Table I.

We consider the results of the similarly treated and more well characterized Ni(II) and Co(II) systems first. In the derivation of the expression for the reciprocal of the relaxation time, τ, simple treatments were first employed, in which the release of a proton upon complexation could be ignored or only the deprotonated form was reacting. These assumptions lead to negative rate constants. Scheme I was then tried, and it led to reasonable results. A general treatment for obtaining relaxation times in metal–ligand systems represented by Scheme I is outlined in the Appendix, and only the main equations for calculating the rate constants are given here. The rate equation for complex formation according to Scheme I is

$$\frac{d[ML^+]}{dt} = k_L[M^{2+}][L^-] - k_{-L}[ML^+] + k_{HL}[M^{2+}][HL] - k_{-HL}[ML^+][H^+] \quad (1)$$

After conservation and rapid equilibrium equations are applied

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(1) Raymond, K.; Carrano, C. *Acc. Chem. Res.* **1979**, *12*, 183–190.

(2) (a) Brown, D.; Chidambaram, M.; Clarke, J.; McAleese, D. *Bioinorg. Chem.* **1978**, *9*, 255–275. (b) Brown, D.; Roche, A.; Pakkanen, T. A.; Pakkanen, T. T.; Smolander, K. *J. Chem. Soc., Chem. Commun.* **1982**, 676–677.

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(9) Eigen, M.; De Maeyer, L. *Tech. Org. Chem.* **1963**, *8*, 975 (Part 2).

(10) Perrin, D.; Sayce, I. *Talanta* **1967**, *14*, 833–842.

(11) Schwarzenbach, G.; Anderegg, G.; L'Eplattenier, F. *Helv. Chim. Acta* **1963**, *46*, 1400–1408.

(12) Liu, C.; Chang, H.; Vang, S.; Sun, P. *J. Chin. Chem. Soc. (Taipei)* **1975**, *22*, 225–235.

and rearranged in a manner similar to Cavasino's treatment of proton-releasing systems,[13] the following expression is obtained:

$$\frac{1}{\tau} = k_{\mathrm{L}}A + \frac{k_{\mathrm{HL}}[\mathrm{H}^+]}{K_{\mathrm{a}}}(A + N) \tag{2}$$

where

$$A = \frac{[\mathrm{M}^{2+}]}{1+\alpha} + [\mathrm{L}^-] + \frac{1}{K_{\mathrm{ML}}}$$

$$N = \frac{[\mathrm{M}^{2+}]}{1+\alpha}\left(\frac{\alpha K_{\mathrm{HL}}}{[\mathrm{H}^+]} + \frac{[\mathrm{L}^-]\alpha}{[\mathrm{H}^+]R} - 1\right)$$

$$\alpha = \frac{[\mathrm{H}^+]}{K_{\mathrm{HL}} + \beta[\mathrm{L}^-]} = \frac{1}{\alpha'} \qquad K_{\mathrm{a}} = \frac{[\mathrm{H}^+][\mathrm{L}^-]}{[\mathrm{HL}]}$$

$$\beta = \frac{K_{\mathrm{In}} + [\mathrm{H}^+]}{K_{\mathrm{In}} + [\mathrm{H}^+] + [\mathrm{In}^-]} \qquad K_{\mathrm{In}} = \frac{[\mathrm{H}^+][\mathrm{In}^-]}{[\mathrm{HIn}]}$$

$$R = 1 + \frac{[\mathrm{In}^-]}{K_{\mathrm{In}} + [\mathrm{H}^+]} \qquad K_{\mathrm{ML}} = \frac{[\mathrm{ML}^+]}{[\mathrm{M}^{2+}][\mathrm{L}^-]}$$

Since N is several magnitudes smaller than A in these solutions, it can be neglected. At constant pH

$$\frac{1}{\tau} \simeq k^{\mathrm{app}}A \tag{3}$$

where

$$k^{\mathrm{app}} = k_{\mathrm{L}} + \frac{k_{\mathrm{HL}}[\mathrm{H}^+]}{K_{\mathrm{a}}}$$

A plot of $1/\tau$ vs. A should give a straight line with slope k^{app} and pass through the origin. The results of the different concentration-dependent experiments at pHs of 6.0, 6.4, and 6.8, for Ni(II) and Co(II), are collected in Tables II and III, respectively. Treatment of the data to yield the apparent rate constants is displayed in Figures 1 and 2. A weighted least-squares computer program was used to determine A. In these plots the only point weighted was the origin. From the values of k^{app} the least-squares program was next used to calculate the specific pH-independent rate constants. Plots of these results are shown in Figures 3 and 4. The slopes of these lines are the rate constants for reaction with the protonated form of the ligand (k_{HL}), and the ordinate intercepts are the rate constants for reaction with the deprotonated form (k_{L}). These specific rate constants and the rate constants for dissociation of the ligand calculated from the known stability constants and measured forward rate constants are colleced in Table IV.

Table II. Ni(II) Relaxation Spectra at 20 °C and Ionic Strength 0.1 M ($NaNO_3$)[a]

$[\mathrm{Ni}^{2+}]_0$, mM[b]	10^5A, M	$10^{-1}/\tau$, s^{-1} obsd	$10^{-1}/\tau$, s^{-1} calcd[f]
		pH 6.0[c]	
1.00	1.62	3.04	2.65
1.50	2.84	5.06	4.65
2.00	4.39	7.50	7.18
2.50	6.25	10.2	10.2
3.00	8.35	13.3	13.7
		pH 6.4[d]	
1.00	2.93	2.49	1.94
1.50	5.27	3.95	3.48
2.00	8.08	5.51	5.34
2.50	12.3	7.48	7.40
3.00	14.6	9.22	9.65
		pH 6.8[e]	
1.00	4.36	1.72	1.27
1.50	7.50	2.47	2.19
2.00	11.0	3.69	3.21
2.50	14.7	4.38	4.29
3.00	18.5	4.83	5.40

[a] Total concentration of metal is equal to twice the total concentration of ligand in all experiments. [b] $[\mathrm{Ni}^{2+}]_0$ = total concentration of Ni(II). [c] Total indicator concentration 2.56×10^{-4} M. [d] Total indicator concentration 1.28×10^{-4} M. [e] Total indicator concentration 9.60×10^{-5} M. [f] Calculated from eq 3.

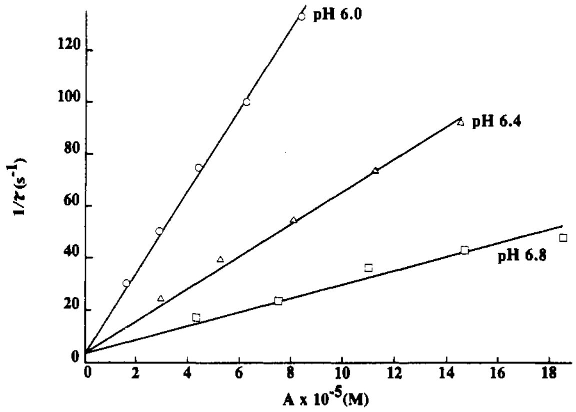

Figure 1. Concentration and hydrogen ion dependence of relaxation times for the Ni(II)–acetohydroxamate system.

Results from the ferrous complex studies were handled differently. Due to the instability of the ferrous complex in the presence of even very small amounts of oxygen around pH 7, these experiments were performed under only one set of conditions. Estimates based on the Ni(II) and Co(II) systems suggested that, under the conditions of our experiments, the observed relaxation time, τ_{obsd}, is dominated by the protonated form of ligand; i.e., we assume $\tau_{\mathrm{obsd}} = \tau_{\mathrm{HL}}$. Comparison of rate constants obtained by this approach for the protonated form of the ligand with Ni(II) and Co(II) led to less than 5% disagreement between the two methods. This treatment prevented us from obtaining the rate constant for the deprotonated form of ligand.

Use of this assumption yields

$$\frac{1}{\tau_{\mathrm{HL}}} = k_{\mathrm{HL}}\left(\frac{[\mathrm{Fe}^{2+}]}{1+\alpha'} + [\mathrm{HL}] + \frac{[\mathrm{FeL}^+]\beta(1+\alpha') + [\mathrm{H}^+]}{K_{\mathrm{stab}}}\right) \tag{4}$$

where α' and β, the terms arising from rapid protolytic equilibria, are the same as the foregoing treatment of Ni(II) and Co(II) and

$$K_{\mathrm{stab}} = \frac{[\mathrm{FeL}^+][\mathrm{H}^+]}{[\mathrm{Fe}^{2+}][\mathrm{HL}]} = K_{\mathrm{ML}}K_{\mathrm{a}}$$

Results of this approach are tabulated in Table IV.

Discussion

Much evidence has been accumulated to indicate that the rate constants with which the second half of the first-row divalent transition-metal ions undergo ligand substitution

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(13) Cavasino, F.; Calvaruso, G.; DiDio, E. *J. Chem. Soc., Dalton Trans.* **1972**, 2632–2637.

Table III. Co(II) Relaxation Spectra at 20 °C and Ionic Strength 0.1 M ($NaNO_3$)[a]

		$10^{-3}/\tau$, s^{-1}	
$[Co^{2+}]_0$, mM[b]	$10^5 A$, M	obsd	calcd[f]
	pH 6.0[c]		
1.00	1.10	2.13	1.67
1.50	3.27	3.22	2.79
2.00	4.99	5.04	4.25
2.50	7.06	5.49	6.02
3.00	9.47	7.81	8.07
	pH 6.4[d]		
1.00	3.44	1.64	1.23
1.50	6.15	2.43	2.19
2.00	9.49	3.66	3.38
2.50	13.3	4.44	4.75
3.00	17.6	6.19	6.28
	pH 6.8[e]		
1.00	5.29	1.20	0.95
1.50	9.24	1.79	1.67
2.00	11.4	2.69	2.49
2.50	18.7	3.10	3.37
3.00	23.9	4.31	4.31

[a] Total concentration of metal is equal to twice the total concentration of ligand in all experiments. [b] $[Co^{2+}]_0$ = total concentration of Co(II). [c] Total indicator concentration 2.56×10^{-4} M. [d] Total indicator concentration 1.28×10^{-4} M. [e] Total indicator concentration 9.60×10^{-5} M. [f] Calculated from eq 3.

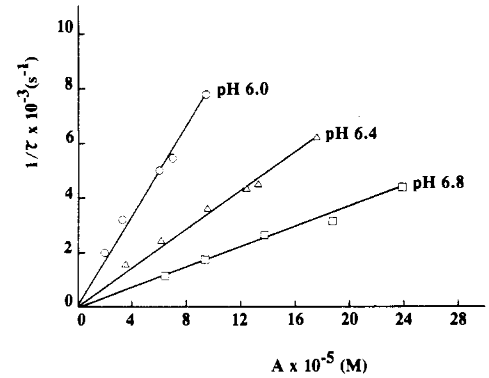

Figure 2. Concentration and hydrogen ion dependence of relaxation times for the Co(II)-acetohydroxamate system.

depend on two factors: (1) the rate constant for release of the coordinated water, which will be replaced by an incoming ligand, and (2) the stability constant for formation of the ligand-metal ion pair.[14,15] The ion pair is the precursor species of the metal-ligand complex, in which the ligand in the vicinity of the metal ion has already lost its relatively loosely held water molecules but the metal ion still retains its coordinated water. This species exists primarily due to electrostatic interactions, and the value of its formation constant is highly dependent on $Z_M Z_L$, the product of the charges on the metal ion and ligand.

Thus, the mechanism of substitution by bidentate ligands is given by Scheme II, where w_1 and w_2 are two water molecules in the metal's inner coordination sphere, the hydroxamate ligand and its two oxygen binding sites are represented by A-A′, and w_2M-A-A represents the monobonded intermediate.

To derive the expression for the experimentally determined rate constants, two assumptions will be made: (1) step IIa

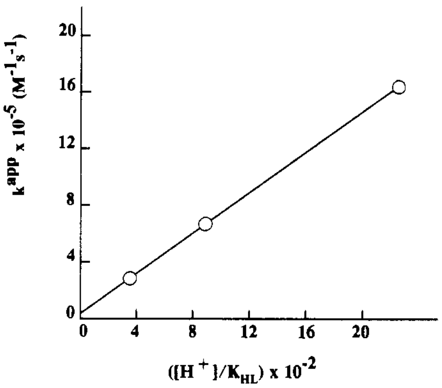

Figure 3. Hydrogen ion dependence of the apparent rate constant for the Ni(II)-acetohydroxamate system.

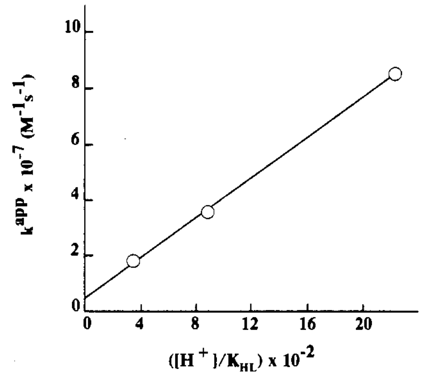

Figure 4. Hydrogen ion dependence of the apparent rate constant for the Co(II)-acetohydroxamate system.

Table IV. Rate Constants for Complex Association and Dissociation[a]

	Fe(II)[b]	Co(II)[c]	Ni(II)[c]
k_L, M^{-1} s^{-1}		$(4.69 \pm 1.17) \times 10^6$	$(3.25 \pm 1.18) \times 10^4$
k_{-L}(exptl), s^{-1}		3.71×10	1.63×10^{-1}
k_{HL}(predicted), M^{-1} s^{-1}	$(6.69 \pm 0.20) \times 10^4$	$(3.59 \pm 0.08) \times 10^4$	$(7.17 \pm 0.08) \times 10^2$
k_{HL}, M^{-1} s^{-1}	4.56×10^5	2.51×10^5	6.48×10^3
k_{-HL}, M^{-1} s^{-1}	2.37×10^9	6.38×10^8	8.03×10^6

[a] Dissociation rate constants obtained from measured forward rate constants and literature values of stability constants as $k_{-L} = k_L/K_{ML}$, and similarly for k_{-HL}. [b] Determined at 10 °C. [c] Determined at 20 °C.

is very rapid with respect to IIb and IIc; (2) $d[w_2M\text{-}A\text{-}A']/dt = 0$. The result[16] is (for L^-, a similar pair of equations can be derived for HL)

$$k_L = k_0 K_{os}\left(\frac{k_0'}{k_{-0} + k_0'}\right) \tag{5a}$$

$$k_{-L} = k_{-0}\left(\frac{k_{-0}'}{k_{-0} + k_0'}\right) \tag{5b}$$

When the rate-limiting step is expulsion of water from the inner coordination sphere and ring closure is much faster, then, in terms of eq 5, $k_0' \gg k_{-0}$, and the expression for the overall rate becomes

$$k_L = k_0 K_{os} \tag{6}$$

We estimate K_{os} from the Eigen-Fuoss equation[17,18] to be 2 M^{-1} for an ion pair of (2+,1−) charge type, assuming spherical

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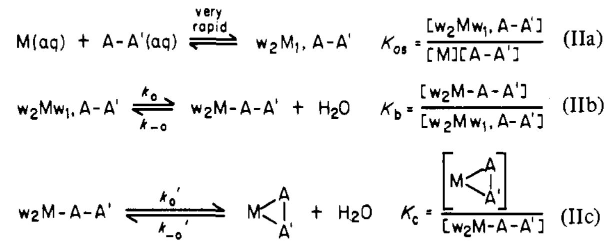
(17) Eigen, M. *Z. Phys. Chem.* (*Wiesbaden*) **1954**, *1*, 176-200.

(18) Fuoss, R. *J. Am. Chem. Soc.* **1958**, *80*, 5059-5061.

Scheme II

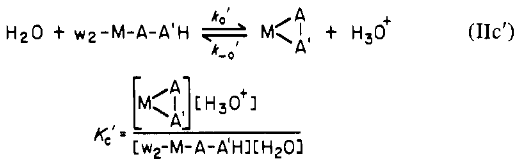


ions of 5-Å diameter. By using water-exchange rates as determined from ^{17}O NMR line broadening[19] to be 1.13×10^6 s^{-1} for Co(II) and 2.8×10^4 s^{-1} for Ni(II) at 298 K, we calculate complex formation rate constants with the anionic form of the ligand to be 2.26×10^6 and 5.5×10^4 M^{-1} s^{-1}, respectively, from eq 6.

These values are in reasonably good agreement with our measured rate constants (Table IV). Although the measured rate constants differ from the theoretically calculated values by about a factor of 2, the limit of accuracy of the Eigen–Fuoss equation is a factor of 2 or 3 and is very sensitive to the choice of the ionic radii. Thus, we conclude that substitution at the Ni(II) and Co(II) centers with this form of ligand follows the Eigen mechanism, with initial attack by the anionic oxygen probable due to electrostatic reasons. For a ligand with this structure there is little reason to anticipate otherwise, as closure to form five-membered rings is generally much faster than water loss.[14]

Complexation with the protonated, neutral form of ligand yields complex formation rate constants that are too small to be attributed to a rate-determining water-loss mechanism. Use of the Eigen–Fuoss equation for an ion pair of charge type (2+,0) predicts an outer-sphere association constant in the vicinity of 0.3 M^{-1}.[20,21] Predicted values of k_{HL} for Fe(II), Co(II), and Ni(II) obtained from the products of k_0K_{os} are calculated in Table IV. All three calculated values are larger than the experimentally determined rate constants by factors of 7–9.

We believe that these results indicate a rate-retarding effect is present when protonated acetohydroxamic acid is the incoming ligand. Furthermore, we ascribe this effect to rate-limiting proton loss on ring closure. This effect may be visualized in terms of the steps presented in Scheme II, by imagining the ligand to be in the protonated form A–A′H, instead of A–A′. Step IIc becomes



This step now includes loss of the second water from the metal, proton loss from the ligand, and ring closure. The introduction of the H^+ term in the right-hand side of step IIc′ makes no difference in the derivation of the expressions for the overall rate constants k_{HL} and k_{-HL}. Thus, if step IIc′ is rate determining, then $k_{-0} > k_0'$ and consequently k_{HL} is smaller than it would otherwise be by the factor $1/(1 + k_{-0}/k_0'[H_2O])$.

Proton transfer is usually diffusion controlled when the free energy change in going from reactants to products is sufficiently large and negative.[22] Viewed as a proton transfer to H_2O, a poor acceptor, an acid dissociation rate constant would be expected to be far below the diffusion-controlled limit, depending on the magnitude of the free energy of dissociation. Therefore, with weak acids in general, and acetohydroxamic acid in particular, where the free energy of proton dissociation is strongly positive (53.1 kJ mol^{-1}; see Table I), the free energy of activation must be at least as great as the overall thermodynamic change in free energy, so that proton transfer to solvent should be a relatively slow reaction.

Table V. Comparison of Rate Constants and M^{2+} Hydrolysis Constants with Enthalpies of Hydration and Ionic Diameters

metal	k_{HL}, M^{-1} s^{-1}	K_{11}, M[a]	ΔH, kJ mol^{-1} [b]	radius, Å[c]
Fe(II)	6.7×10^4	3.16×10^{-10}	−2850	0.76
Co(II)	3.6×10^4	6.31×10^{-11}	−2900	0.74
Ni(II)	7.2×10^2	3.16×10^{-11}	−2980	0.69

[a] $K_{11} = [MOH^+][H^+]/[M^{2+}]$, 298 K, ionic strength 1.0 M ($NaClO_4$) from: Baes, C.; Mesmer, R. "The Hydrolysis of Cations"; Interscience: New York, 1976. [b] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972; p 594. [c] *Ibid.*, p 52. These are Pauling ionic radii.

It is therefore constructive to compare the rate constant for proton loss from uncomplexed acetohydroxamic acid with that from the monobonded complex in step IIc′. By utilizing reaction III (Scheme III), the rate constant for proton loss from uncomplexed HL can be calculated from the acid dissociation constant, K_a, the concentration of water, 55.5 M, and the rate constant for recombination of proton and ligand conjugate base, assuming that the latter, thermodynamically favorable process is diffusion controlled. Then, $k_{-H} = 55.5K_a\,k_H \approx (55.5\ M)(5 \times 10^{-10}\ M^{-1})(5 \times 10^{10}\ M^{-1}\ s^{-1}) \cong 1.4 \times 10^3\ M^{-1}\ s^{-1}$. This rate constant is smaller than the experimentally determined complex formation rate constant for Co(II) and Fe(II) and comparable to that for Ni(II).

Scheme III

$$H_2O + HL \underset{k_H}{\overset{k_{-H}}{\rightleftharpoons}} H_3O^+ + L^- \qquad (III)$$

$$55.5K_a = k_{-H}/k_H$$

Two effects can combine to enhance proton loss in the monobonded complex relative to that for the free acid. First, in the monobonded complex, where the carbonyl oxygen is bonding to the metal,[23] the proton may be lost more readily than in the free acid, due to the metal–proton repulsion. Second, the electron density on the anion may be decreased by inductive electron flow into the electron-deficient metal center through the π-conjugated ligand system. This effect lowers the activation energy for loss of the proton.

The k_{HL} rate constant is observed to decrease in the order Fe(II) > Co(II) > Ni(II). Likewise, the ease of hydrolysis follows the same order (Table V). However, the charge to volume ratios and M^{2+} enthalpies of hydration for these three ions follow the opposite trend. As an explanation of how these opposing trends affect the kinetics and thermodynamics of proton removal from the ligand, we suggest that the decreasing availability of π acidity as one proceeds from Fe(II) ($^1t_{2g}$) to Ni ($^6t_{2g}$) is responsible for the observed kinetic trend. Thus, Fe(II), with the most electron orbital vacancy of the three, exhibits the fastest rate and Ni(II), with no orbital vacancies to interact with ligand π electrons, exhibits the lowest rate.

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In terms of this explanation, metal–proton repulsion is not the dominant factor, and k_{HL} for Ni(II) closely approaches the free ligand acid dissociation rate constant.

It is also possible to explain our observations of reduced rate constants for complexation with the protonated form of ligand as resulting from intramolecuar hydrogen bonding within the ligand. We cannot eliminate this possibility; however, conclusions from other studies with ligands capable of intramolecular hydrogen bonding[24–26] cast some doubt on this interpretation. These previous studies report decreases ranging from fifty- to several hundred-fold with ligands possessing pK's much larger than that of acetohydroxamic acid. A stronger acid such as ours would be expected to exhibit a smaller effect, as observed.

However, other observations are not consistent. All ligands studied so far have been observed to react via direct attack at the hydrogen-bonded atom, oxygen or nitrogen. The relative insensitivity of our ligand to the attacking metal ion argues for a second, never observed, possibility: selective reaction with only a reactive open form (HL*), which is in rapid equilibrium with the unreactive hydrogen-bonded from (HL). It seems quite unlikely that acetohydroxamic acid, with a weaker hydrogen bond than the other ligands, should be relatively less reactive than they are in the open form.

The bimolecular reverse rate constants, k_{-HL}, should not exceed the diffusion-limited value for a "+,+" reaction encounter where one of the reacting partners is the proton. We take as a typical value of such a diffusion-controlled rate constant the value for the reaction $UO_2(OH)^+ + H^+$, which is 1.6×10^{10} M^{-1} s^{-1}.[27] Only the ferrous complex rate constant approaches this value, being well below at about one-seventh the theoretical value.

Rate constants for reaction of HL with Fe^{3+} and $FeOH^{2+}$ have been determined for mono complex formation,[4] and for bis and tris complex formation as well.[5] To be sure, the forward and reverse mono complex rate constants for iron(III) are much less than those of iron(II), viz., 1.2 vs. 6.69×10^4 M^{-1} s^{-1}. (For $FeOH^{2+}$ the value jumps to 2×10^3 M^{-1} s^{-1}.) However, the bimolecular substitution rate constant with Fe^{3+} is typical of the value found for reaction with uncharged monodentate ligands. Consequently, in the iron(III) system, where the metal–proton repulsion is greater, ring closure is rapid relative to formation of the monobonded intermediate complex, but in iron(II) the two steps are competitive due to rate-limiting proton loss.

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Appendix

After a small perturbation, close to equilibrium, relation A1

$$[X] = [X]_e + \Delta[X] \qquad \text{(A1)}$$

holds for all species, X, in solution, where the subscript "e" refers to equilibrium and $\Delta[X] \ll [X], [X]_e$. Substituting (A1) into (1), expanding, neglecting terms quadratic in $\Delta[X]$, and utilizing the equilibrium relation that

$$\frac{d[ML^+]_e}{dt} = \frac{d[M^{2+}]_e}{dt} = \frac{d[H^+]_e}{dt} = \frac{d[HL]_e}{dt} = \frac{d[L^-]_e}{dt} = 0$$

we obtain (A2):

$$\frac{d[\Delta[ML^+]]}{dt} = -\frac{\Delta[ML^+]}{\tau} = k_L([M^{2+}]_e(\Delta[L^-]) + [L^-]_e(\Delta[M^{2+}])) + k_{HL}([M^{2+}]_e(\Delta[HL]) + [HL]_e(\Delta[M^{2+}])) - k_{-L}(\Delta[ML^+]) - k_{-HL}([M^{2+}]_e(\Delta[H^+]) + [H^+]_e(\Delta[ML^+])) \qquad \text{(A2)}$$

Additional relations are

$$K_{c1} = \frac{k_L}{k_{-L}} \qquad \text{(A3a)}$$

$$K_{c2} = \frac{k_{HL}}{k_{-HL}} \qquad \text{(A3b)}$$

$$\Delta[M^{2+}] = -\Delta[ML^+] \qquad \text{(A4a)}$$

$$\Delta[L^-] + \Delta[HL] = -\Delta[ML^+] \qquad \text{(A4b)}$$

$$\Delta[H^+] + \Delta[HL] + \Delta[HIn] = 0 \qquad \text{(A4c)}$$

$$\Delta[HIn] = -\Delta[In^-] \qquad \text{(A4d)}$$

With use of the mass-action relations (A3) and mass-balance relations (A4), eq A2 becomes eq A5. Addition and sub-

$$\frac{1}{\tau} = k_L\left(\frac{[M^{2+}]}{1 + \alpha} + [L^-] + \frac{1}{K_{c1}}\right) + k_{HL}\left(\frac{[M^{2+}]}{1 + \alpha'} + [HL] + \frac{1}{K_{c1}K_a}\frac{[ML^+]}{R(1 + \alpha')} + [H^+]\right) \qquad \text{(A5)}$$

traction of the appropriate terms in the rate constant coefficients then yield eq 2.

Registry No. Acetohydroxamic acid, 546-88-3; Fe, 7439-89-6; Co, 7440-48-4; Ni, 7440-02-0.

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